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(54) **Process for the hydroisomerization of Fischer-Tropsch wax to produce lubricating oil.**

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Description

BACKGROUND OF THE INVENTION

I. Field of the Invention

This invention relates to a process for producing lubricating oil from a Fischer-Tropsch wax. More particularly, it relates to a process utilizing a Group VIII metal-on-alumina catalyst for hydroisomerizing a hydrotreated Fischer-Tropsch wax to produce a lubricating oil having a high viscosity index and a low pour point.

II. Description of the Prior Art

In the Fischer-Tropsch process a synthesis gas ($CO + H_2$) made, e.g., from natural gas, is converted over a catalyst, e.g., a ruthenium, iron or cobalt catalyst, to form a wide range of products inclusive of gaseous and liquid hydrocarbons, and oxygenates, and a normally solid paraffin wax which does not contain the sulfur, nitrogen or metals impurities normally found in crude oil. It is generally known to catalytically convert the paraffin wax, or syncrude obtained from such process to lower boiling paraffinic hydrocarbons falling within the gasoline and middle distillate boiling ranges.

Paraffin waxes have been isomerized over various catalysts, e.g., Group VIB and VIII catalysts of the Periodic Table of the Elements (E. H. Sargent & Co., Copyright 1964 Dyna-Slide Co.) Certain of such catalysts can be characterized as halogenated supported metal catalysts, e.g., a hydrogen chloride or hydrogen fluoride treated platinum-on-alumina catalyst as disclosed, e.g., in U.S. 2,668,866 to G. M. Good et al. In the Good et al. process a partially vaporized wax, such as one from a Fischer-Tropsch synthesis process, is mixed with hydrogen and contacted at 300°C to 500°C over a bed of supported platinum catalyst. Palladium or nickel may be substituted for platinum. The support may be a number of conventional carrier materials, such as alumina or bauxite. The carrier material may be treated with acid, such as HCl or HF, prior to incorporating the platinum. In preparing the catalyst, pellets of activated alumina may be soaked in a solution of chloroplatinic acid, dried and reduced in hydrogen at 475°C.

U.S. Patent No. 2,817,693 discloses the catalyst and process of U.S. Patent No. 2,668,866 with the recommendation that the catalyst be pretreated with hydrogen at a pressure substantially above that to be used in the process.

U.S. Patent No. 3,268,439 relates to the conversion of waxy hydrocarbons to give products which are characterized by a higher isoparaffin content than the feedstock. Waxy hydrocarbons are converted at elevated temperature and in the presence of hydrogen by contacting the hydrocarbons with a catalyst comprising a platinum group metal, a halogenatable inorganic oxide support and at least one weight percent of fluorine, the catalyst having been prepared by contacting the support with a fluorine compound of the general formula:

$$\begin{array}{c} F \\ | \\ Y-X-F \\ | \\ Y \end{array}$$

where X is carbon or sulphur and Y is fluorine or hydrogen.

U.S. Patent No. US-A-3,308,052 describes a hydroisomerization process for producing lube oil and jet fuel from wary petroleum fractions. According to this patent, product quality is dependent upon the type of charge stock, the amount of liquid hydrocarbon in the waxy charge stock and the degree of conversion to material boiling below 650°F (343°C). The greater the amount of charge stock converted to material boiling below 650°F (343°C) per pass the higher the quality of jet fuel. The catalyst employed in the hydroisomerization zone is a platinum group metal catalyst comprising one or more platinum, palladium and nickel on a support, such as alumina, bentonite, barite, faujasite, etc., containing chlorine and/or fluorine.

In U.S. Patent No. US-A-3,365,390 a heavy oil feed boiling at least partly above 900°F (482.2°C) is hydrocracked and the oil effluent thereof is separated into fractions, including a distillate fuel and a higher boiling hydrocracked lube oil boiling range fraction. The hydrocracked lubricating oil boiling range fraction is dewaxed to obtain a hydrocracked wax fraction which is hydroisomerized in the presence of a reforming

catalyst and the oil effluent thereof is separated into fractions, including a distillate fuel and an isomerized lube oil boiling range fraction.

In U.S. Patent No. US-A-3,486,993 the pour point of a heavy oil is lowered by first substantially eliminating organic nitrogen compounds present in the oil and then contacting the nitrogen-free oil with a reforming catalyst in a hydrocracking-hydroisomerization zone. Hydroisomerization is conducted at a temperature of 750°F-900°F (398.9-482.2°C) over a naphtha reforming catalyst containing no more than two weight percent halide.

U.S. Patent No. US-A-3,487,005 discloses a process for the production of low pour point lubricating oils by hydrocracking a high pour point waxy oil feed boiling at least partly above 700°F (371.1°C) in at least two stages. The first stage comprises a hydrocracking-denitrofication stage, followed by a hydrocracking-isomerization stage employing a naphtha reforming catalyst containing a Group VI metal oxide or Group VIII metal on a porous refractory oxide, such as alumina. The hydrocracking isomerization catalyst may be promoted with as much as two weight percent fluorine.

U.S. Patent No. US-A-3,709,817 describes a process which comprises contacting a paraffin hydrocarbon containing at least six carbon atoms with hydrogen, a fluorided Group VIB or VIII metal alumina catalyst and water. These catalysts are classified by the patentee as a well-known class of hydrocracking catalysts.

III. Summary of the Invention

A process for producing a lubricating oil having a high viscosity index and a low pour point from a Fischer-Tropsch wax which process is in accordance with claim 1, and which comprises:

(a) contacting the Fischer-Tropsch wax with a hydrotreating catalyst and hydrogen to reduce the oxygenate and trace metal levels of the wax and to partially hydrocrack/isomerize the wax;

(b) contacting the hydrotreated Fischer-Tropsch wax from step (a) with hydrogen in a hydroisomerization zone in the presence of a fluorided Group VIII metal-on-alumina catalyst having (i) a bulk fluoride concentration ranging from 2 to 10 weight percent, wherein the fluoride concentration is less than about 3.0 weight percent at the outer surface layer to a depth less than one one hundredth of an inch (0.254mm) provided the surface fluoride concentration is less than the bulk fluoride concentration, (ii) an aluminum fluoride hydrate level greater than 60 where an aluminum fluoride hydrate level of 100 corresponds to the X-ray diffraction peak height of 5.66Å (0.566nm) for a Reference Standard;

(c) fractionating the effluent from step (b) to produce a lubricating oil fraction boiling at atmospheric pressure above 640°F (337.8°C), preferably above 700°F (371.1°C); and

(d) dewaxing the lubricating oil fraction from step (c) to produce a dewaxed lubricating oil having a viscosity index of at least 130 and a pour point less than about 0°F (-17.8°C).

In preferred embodiments, the hydrotreating catalyst will be unsulfided, the catalyst employed in the hydroisomerization zone will be a fluorided platinum-on-aluminum catalyst, and the isomerate is contacted with hydrogen in the presence of a hydrogenation catalyst to reduce unsaturation of the isomerate and thereby improve its daylight and oxidation stability.

IV. Brief Description of the Drawing

The Figure schematically depicts a process of the invention for the production of a lubricating oil boiling substantially in the range of about 700°F (371.1°C) to 1050°F (565.6°C) from a Fischer-Tropsch wax.

V. Description of the Preferred Embodiments

In accordance with the invention, a Fischer-Tropsch wax is hydrotreated under relatively high severity conditions to remove impurities and partially convert the 1050°F+ (565.6°C+) wax, followed by hydroisomerisation of the hydrotreated wax, hydrofining of the isomerate to improve daylight stability, fractionation to recover a lubricating oil fraction, and dewaxing to produce a high viscosity, low pour point lubricating oil.

Fischer-Tropsch wax may be made as a by-product from the conversion of natural gas or gasification of coal under known conditions to a synthesis gas ($Co+H_2$) which may then be converted by the Fischer-Tropsch process to form gaseous and liquid hydrocarbons and a normally solid paraffin wax known as Fischer-Tropsch wax. This wax does not contain the sulfur, nitrogen or metal impurities normally found in crude oil, but is known to contain water, trace metals and a number of oxygenate compounds such as alcohols, ketones, aldehydes, etc. These oxygenate compounds have an adverse effect on the performance of the hydroisomerization/hydrocracking catalyst of the invention and it is, therefore, advantageous to

produce lube oil products by the process scheme outlined in the Figure.

Referring to the Figure, a Fischer-Tropsch wax is introduced into Hydrotreater R-1 along with hydrogen and contacted therein with a hydrotreating catalyst. Fischer-Tropsch wax is generally composed of about 99+% normal paraffins, with trace amounts of metals and oxygenates as impurities. It is all high melting wax, and requires considerable structural modification (normal paraffin wax is first converted to iso-paraffin wax before oil is produced). Hydrotreating serves a dual purpose, namely, removal of the impurities and conversion of some of the Fischer-Tropsch wax, particularly the fraction boiling above 1050°F (565.6°C). Hydrotreating mild conditions removes impurities in the Fischer-Tropsch wax, but more severe hydrotreating conditions are preferred in the process of the present invention in order to convert some of the higher boiling Fischer-Tropsch wax. This is in contrast, for example, to a petroleum slack wax which normally contains some relatively low melting wax which needs only a slight reduction in pour point to become oil. In the case of petroleum slack waxes relatively mild hydrotreating conditions are employed to remove nitrogen and sulfur, while avoiding conversion of the naphthenes and isoparaffins present in the slack wax.

It has been found advantageous, therefore, to employ relatively severe hydrotreating conditions in Hydrotreater R-1 in order to remove impurities and soften the Fischer-Tropsch wax prior to hydroisomerization. These conditions include a temperature in the range of from 650°F to 775°F (343.3 to 412.8°C), preferably 700°F to 750°F (371.1 to 398.9°C), a hydrogen pressure between about 500 and 2500 psig (pounds per square inch gauge) (3.448 to 17.238 MPa), preferably between 1000 and 1500 psig (6.895 to 10.343 MPa), a space velocity of between 0.1 and 2.0 V/V/Hr (volume of feed/volume of catalyst per hour), preferably 0.2 and 0.5 V/V/Hr, and a hydrogen gas rate between 500 and 5000 SCF/B (standard cubic feet of hydrogen per barrel of feed) (89.05 to 890.47 liter H_2/liter feed), preferably between 1000 and 2000 SCF/B (178,1 to 356,2 liter H_2/liter feed). The hydrotreating catalyst includes the well known hydrotreating catalysts such as Co/Mo or Ni/Mo on alumina. Other hydrotreating catalysts include combination of Co and/or Ni and Mo and/or W on a silica/alumina base. Typically such hydrotreating catalysts are presulfided, but it is preferred to employ a non-sulfided hydrotreating catalyst in R-1.

The hydrotreated Fischer-Tropsch wax from R-1 is introduced into Hydroisomerization Reactor R-2 along with fresh hydrogen or dewatered recycle hydrogen and contacted therein under hydroisomerization conditions with a fluorided Group VIII metal-on alumina catalyst.

Hydroisomerization is carried out at temperatures ranging between 500°F (260°C) and 750°F (398.9°C), preferably from 600°F to 725°F (315.6 to 385°C), at a feed space velocity of from about 0.2 to 2.0 V/V/Hr., preferably from about 0.5 to 1.0 V/V/Hr. Pressure is maintained at from 500 to 2500 psig (3.45 to 17.24 MPa), preferably from 1000 to 1500 psig (6.895 to 10.343 MPa), and hydrogen is fed into the reacter at a rate of about 500 to 10,000 SCF/B (89.05 to 178.09 liter H_2/liter feed), preferably about 2000 to 6000 SCF/B (356,2 to 1068,6 liter H_2/liter feed). The conditions in hydroisomerization reactor R-2 are preferably selected to convert from 10 to 35 weight percent (wt.%), preferably 15 to 30 wt% to distillate and lighter (650°F-,343.3°C), of the hydrotreated Fischer-Tropsch wax delivered to R-2. It has been found that such conversion in the 15 to 30 percent range maximizes the production of the desired lubricating oil product.

The catalyst employed in hydroisomerization reactor R-2 is a particulate fluorided Group VIII metal-on-alumina catalyst composition where Group VIII refers to the Periodic Table of Elements (E. H. Sargent & Co., Copyright 1964 Dyna-Slide Co.). Platinum is the preferred Group VIII metal. Alumina is the catalyst base and for purposes of this invention alumina includes alumina-containing materials such as silica alumina and the like.

The fluorided Group VIII metal-on-alumina catalyst comprises from 0.1 to 2 percent, preferably from 0.3 to 0.6 percent Group VIII metal and from 2 percent to 10 percent fluoride, preferably from 5 percent to 8 percent fluoride, based on the total weight of the catalyst composition (dry basis), such fluoride concentration being herein referred to as the bulk fluoride concentration.

The particulate catalyst of the invention will have a fluoride concentration less than about 3.0 weight percent, preferably less than 1.0 weight percent and most preferably less than 0.5 weight percent at its outer surface layer, provided the surface fluoride concentration is less than the bulk fluoride concentration. The outer surface layer is measured to a depth less than one one hundredth of an inch (0.254mm). The surface fluoride was measured by scanning electron microscope. The remaining fluoride is distributed with the Group VIII metal at a depth below the outer shell into and within the particle interior.

The fluoride content of the catalyst can be determined in a number of ways.

One technique analyzes the fluorided catalyst using oxygen combustion methodology which is well established in the literature. Approximately 8-10 mg of sample is mixed with 0.1 g benzoic acid and 1.2 gm of mineral oil in a stainless steel combustion capsule which is mounted in a 300 mL. Parr oxygen combustion bomb. The "sample" is purged of air and subsequently combusted under 30 Atms of pure

oxygen. Combustion products are collected in 5 mL. of deionized water. Once the reaction has gone to completion (about 15 minutes), the absorbing solution is quantitatively transferred and made to fixed volume.

Fluoride concentration of the sample is determined by ion chromatography analysis of the combustion product solution. Calibration curves are prepared by combusting several concentrations of ethanolic KF standards (in the same manner as the sample) to obtain a 0-10 ppm calibration range. Fluoride concentration of the catalyst is calculated on an ignition-loss-free-basis by comparison of the sample solution response to that of the calibration curve. Ignition loss is determined on a separate sample heated to 800 degrees F (426.7°C) for at least 2 hours. Ion chromatographic analysis uses standard anion conditions.

Another procedure employs the use of fluoride distillation with a titrimetric finish. Fluorides are converted into fluorosilicic acid (H_2SiF_6) by reaction with quartz in phosphoric acid medium, and distilled as such using super heated steam. This is the Willard-Winter-Tananaev distillation. It should be noted that the use of super heated, dry (rather than wet) steam is crucial in obtaining accurate results. Using a wet stern generator yielded results 10-20% lower. The collected fluorosilicic acid is titrated with standardized sodium hydroxide solution. A correction has to be made for the phosphoric acid which is also transferred by the steam. Fluoride data are reported on an ignition-loss-free-basis after determination of ignition loss on sample heated to 400 degree C for 1 hour.

The platinum contained on the alumina component of the catalyst will preferably have an average crystallite size of up to 50Å (5nm), more preferably below about 30Å (3nm).

The preferred catalyst of the invention will be relatively free of nitrogen and, accordingly, the catalyst will have a nitrogen/aluminum (N/Al) ratio less than about 0.005, preferably less than about 0.002, and most preferably less than about 0.0015.

The catalyst used in the hydroisomerization reactor R-2 will have high intensity peaks characteristic of aluminum fluoride hydroxide hydrate as well as the peaks normally associated with gamma alumina. X-ray diffraction data (X-ray Diffractometer, Scintag U.S.A.) show that the fluoride present in the preferred catalyst will be substantially in the form of aluminum fluoride hydroxide hydrate. This catalyst is described in detail in co-pending application OP-3402 filed in the names of Glen P. Hamner and Willard H. Sawyer.

The relative X-ray diffraction peak height at 2θ = 5.66Å (0.566nm) is taken as a measure of the aluminum fluoride hydroxide hydrate content of the catalyst. The 5.66Å (0.566nm) peak for the Reference Standard is taken as a value of 100. For example, fluorided platinum-on-alumina catalyst having a hydrate level of 60 would therefore have a 5.66Å (0.566nm) peak height equal to 60% of the 5.66Å (0.566nm) peak height of the Reference Standard, with a value of 80 corresponding to a catalyst having a 5.66Å (0.566nm) peak height equal to 80% of the 5.66Å (0.566nm) peak height of the Reference Standard etc. The catalyst used in reactor R-2 will have a hydrate level of at least 60, preferably at least 80, and most preferably at least about 100.

The Reference Standard contains 0.6 wt% Pt and 7.2 wt% F on γ alumina having a surface area of about 150 m^2/g. The Reference Standard is prepared by treatment of a standard reforming grade platinum on alpha alumina material containing 0.6 wt% Pt on 150 m^2/g surface area γ alumina with platinum, followed by single contact with an aqueous solution containing a high concentration of hydrogen fluoride (e.g., 10-15 wt% HF solution such as 11.6 wt% HF solution) with drying at 300°F (148.9°C) in accordance with the following procedure.

The catalyst employed in R-2 may be prepared in the following manner. The Group VIII metal, preferably platinum, can be incorporated with the alumina in any suitable manner, such as by coprecipitation or co-gellation with the alumina support, or by ion exchange with the alumina support. In the case of a fluorided platinum-on-alumina catalyst, a preferred method for adding the platinum group metal to the alumina support involves the use of an aqueous solution of a water soluble compound, or salt of platinum to impregnate the alumina support. For example, platinum may be added to the support by co-mingling the uncalcined alumina with an aqueous solution of chloroplatinic acid, ammonium chloroplatinate, platinum chloride, or the like, to distribute the platinum substantially uniformly throughout the particle. Following the impregnation, the impregnated support can then be dried and subjected to a high temperature calcination, generally at a temperature in the range from 700°F (371.1°C) to 1500°F (815.6°C), preferably from 850°F to 1300°F (454 to 704.4°C), generally by heating for a period of time ranging from 1 hour to 20 hours, preferably from 1 hour to 5 hours. The platinum component added to the alumina support, is calcined at high temperature to fix the platinum thereupon prior to adsorption of a fluoride, suitably hydrogen fluoride or hydrogen fluoride and ammonium fluoride mixtures, into the platinum-alumina composite. Alternatively the solution of a water soluble compound, or salt of platinum can be used to impregnate a pre-calcined alumina support, and the platinum-alumina composite again calcined at high temperature after incorporation of the platinum.

The Group VIII metal component is substantially uniformly distributed throughout a precalcined alumina support by impregnation. The Group VIII metal-alumina composite is then calcined at high temperature, and the fluoride, Preferably hydrogen fluoride, is distributed onto the precalcined Group VIII metal-alumina composite in a manner that most of the fluoride Will be substantially composited at a level below the outer surface of the particles.

The catalyst having the fluoride substantially in the form of aluminum fluoride hydroxide hydrate is preferably prepared in the following manner. The platinum is distributed, generally substantially uniformly throughout a particulate alumina support and the platinum-alumina composite is calcined. Distribution of the fluoride on the catalyst, preferably hydrogen fluoride, is achieved by a single contact of the precalcined platinum-alumina composite with a solution which contains the fluoride in sufficiently high concentration. preferably an aqueous solution containing the fluoride in high concentration is employed, a solution generally containing from 10 percent to 20 percent, preferably from 10 percent to 15 percent hydrogen fluoride. Solutions containing hydrogen fluoride in these concentrations will be adsorbed to incorporate most of the hydrogen fluoride, at an inner layer below the outer surface of the platinum-alumina particles.

The platinum-alumina composite, after adsorption thereupon of the fluoride component is heated during preparation to a temperature ranging up to but not exceeding 650°F (343.3°C), preferably about 500°F (260°C), and more preferably 300°F (148.9°C). Where a HF/NH_4F solution is used to incorporate the fluoride, the catalyst is dried at a temperature ranging up to but not exceeding about 850°F (454.4°C). A characteristic of the inner platinum-fluoride containing layer is that it contains a high concentration of aluminum fluoride hydroxide hydrate. It can be shown by X-ray diffraction data that a platinum-alumina catalyst formed in such manner displays high intensity peaks characteristic of both aluminum fluoride hydroxide hydrate and gamma alumina.

The isomerate from R-2 may be fractionated and then dewaxed or it may first be introduced with hydrogen into hydrofinishing reactor R-3 containing a hydrogenation catalyst to hydrogenate the unsaturates present in the isomerate product and thereby improve its daylight stability. The reactor conditions are relatively mild and include, for example a temperature in the range of about 340-450°F (171.1-232.2°C), preferably about 365°F (185°C) to 425°F (218.3°C), at pressures of about 300 to 1500 psi H_2, preferably 500 to 1000 psi H_2, a gas rate of 500 to 10,000 SCF/B (89.05 to 1780.94 liters H_2/liter feed), preferably 1000 to 5000 SCF/B (178.09 to 890.47 liters H_2/liter feed) and a space velocity of about 0.25 to 20 V/V/Hr., preferably about 1-4 V/V/Hr.

The catalyst employed in R-3 includes, for example, the hydroisomerization catalyst employed in R-2 or a noble Group VIII metal on a refractory metal oxide such as alumina, silica-alumina and the like.

The effluent from R-3 is fractionated in distillation tower F-1 to produce an overhead light end product boiling below 640°F (337.8°C), a lubricating oil fraction boiling in the range of 640°F - 1000°F (337.8-537.8°C), preferably in the range of 700°F - 900°F (371.1-482.2°C) and a residual fraction. The lubricating oil fraction is then introduced into the dewaxing zone D-1 where unconverted wax is removed to result in a lubricating oil having a viscosity index of at least 130, preferably a viscosity index greater than 140, and a pour point no greater than 0°F (-17.8°C) and preferably a pour point below -6°F (-21.1°C). The residual fraction from F-1 will typically have an initial boiling point it atmospheric pressure above 1000°C and will be recycled with the wax from D-1 to the hydroisomerization reactor R-2.

Dewaxing in D-1 is accomplished by techniques which permit the recovery of unconverted wax, since, as indicated, this unconverted wax is recycled to the hydroisomerization unit. Solvent dewaxing is utilized in D-1 and employs typical dewaxing solvents. Solvent dewaxing utilizes typical dewaxing solvents such as C_3-C_6 ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C_6-C_{10} aromatic hydrocarbons (e.g. toluene) mixtures of ketones and aromatics (e.g. MEK/toluene), autorefrigerative solvents such as liquified, normally gaseous C_3-C_4 hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof, etc. at filter temperature of -18°F to -22°F (-27.8 to -30°C). The isomerate may be dewaxed under miscible conditions with a high yield of dewaxed oil at a high filter rate with a mixture of MEK/MIBK (20/80) used at a temperature in the range -18°F to 122°F (-27.8 to -30°C). Pour points lower than -6°F (-21.1°C) can be achieved using lower filter temperatures and other ratios of said solvent but a penalty may be paid due to operation under immiscible conditions, the penalty being lower filter rates.

The invention is further illustrated by the following examples.

Example

A synthetic hydrocarbon wax (Fischer-Tropsch source) feed was obtained as a 700°F+ (371.1°C+) fraction by the distillation of a total Fischer-Tropsch synthesis product. The synthesis wax feed had the following properties:

Melting Point, (°F) °C	(>220) >104.4°C
Oil Content, wt%	nil
Sulfur, ppm	nil
Nitrogen, ppm	nil
Oxygen, wt%	0.34
Metals (Fe,Co)	trace

The wax feed was hydroisomerized over a platinum on fluorided alumina catalyst having the following composition:

Platinum concentration, wt%	0.58
Platinum Cystallite size (Å) nm	(26) 2.6
Fluorine, wt%	7.9
Aluminum Fluoride Hydroxide Hydrate level intensity at 5.66Å (0.566nm) (X-ray diffraction)	250
Nitrogen/Al_2O_3 Atomic Ratio	0.005
Surface area, m^2/g	138
Pore volume, cm^3/g	0.42

The catalyst was reduced with hydrogen at 650°F (343.3°C) for two hours prior to introducing the 700°F+ (371.1°C) wax feed with hydrogen.

Process conditions for the hydroisomerization and the dewaxing operation with isomerate (700°F+, 371.1°C) so produced are given in Table I with the corresponding dewaxed oil properties.

Table I

Table I

Dewaxed Oils from Fischer-Tropsch Hydroisomerization

Isomerization Conditions		
Temperature, (°F) °C	(708) 375.6	(716) 380
V/V/Hr.	1	
Pressure, (psi) MPa	(1000) 6.895	
Treat Gas, (SCF H_2/bbl) Liter H_2/Liter feed	(2500) 445.24	
Conversion to 700°F-(371.1°C-), wt%	13	19
Isomerate (700°F+, 371.1 °C +) Feed to Dewaxing		
Cloud Point, (°F) °C	(208) 97.8 °C	(187) 86.1
Viscosity, cs (at 210°F) (at 98.9 °C)	7.3	6.5
Dewaxing Conditions		
Solvent:	40/60 MEK/Toluene	
Diluent-Oil Ratio	4 to 1	
Filter Temperature (°F) °C	(-22) -30 °C	
Dewaxed Oil Properties		
Pour Point (°F) °C	(9) -12.8 °C	(-4) -20 °C
Viscosity, cs at 100°F, 37.8 °C	39	33.8
at 210°F, 98.9 °C	7.5	6.7
Viscosity Index	163	159
Wax Recovered, wt%	48	30
Theoretical Dewax Oil Yield wt%	52	70

It is apparent that at low levels of wax conversion and when using typical dewaxing solvents under standard conditions (filter temperature -22°F, -30°C), a low yield of dewaxed oil having an unsatisfactory pour point is produced. Lower filtration temperatures would produce the desired pour point but would produce an even lower dewax oil yield. Hydroisomerization at a higher level of conversion (e.g. 30% wax remaining in the isomerate 700°F+ 371.1°C+) facilitates the production of a lower pour point product within the conventional dewaxing parameters employed in dewaxing plants. A major portion of the unconverted wax is associated with the 1050°F+ (565.6°C+) isomerate and thus the recycle of this fraction to the isomerization zone would be the preferred method of reducing the wax load to the dewaxing operation, as well as increasing the overall yield of oil from wax.

Our patent application, reference No. OP-3402, referred to herein, refers to our European patent application No. 88311981.0 (claiming Convention priority of our U.S. patent application Serial No. 134,796 filed on 18 December 1987) entitled "Catalyst (and its Preparation) for Wax Hydroisomerization and Hydrocracking to produce Liquid Hydrocarbon Fuels" and which describes and claims a particulate fluorided Group VIII metal-on-alumina catalyst having: (a) a Group VIII metal concentration ranging from about 0.1 to about 2 weight percent; (b) a bulk fluoride concentration in the range of from about 2 to about 10 weight percent, wherein the fluoride concentration is less than about 3.0 weight percent at the outer surface layer to a depth less than one one-hundredth of an inch (0.254 mm), provided the surface fluoride concentration is less than the bulk fluoride concentration; (c) an aluminum fluoride hydroxide hydrate level greater than 60 where an aluminum fluoride hydroxide hydrate level of 100 corresponds to the X-ray diffraction peak height at 5.66Å (0.566 nm) for a Reference standard; and (d) a N/Al ratio less than about 0.005 (e.g., less than 0.002).

Claims

1. A process for producing a lubricating oil having a high viscosity index and a low pour point from a Fischer-Tropsch wax, which process comprises:
(a) contacting the Fischer-Tropsch wax with a hydrotreating catalyst (which may be unsulfided) and hydrogen in a hydrotreating zone (R-1) under hydrotreating conditions (comprising a temperature in the range 650 to 775°F (343.3 to 412.8°C), a hydrogen pressure in the range 500 to 2500 psig (3.448 to 17.238 MPa), a space velocity in the range 0.1 to 2.0 v/v/h and a hydrogen to feed rate in the range 500 to 5000 SCF/B (89.04 to 890.44 liters H_2 per liter feed)) to reduce the oxygenate and trace metal levels of the wax and to partially hydrocrack and isomerize the wax;
(b) contacting the hydrotreated Fischer-Tropsch wax from step (a) with hydrogen under hydroisomerisation conditions (comprising a temperature in the range of from 500 to 750°F (260 to 398.9°C), a feed space velocity in the range of from 0.2 to 2.0 v/v/h, a gauge pressure in the range of from 500 to 2500 psig (3.448 to 17.238 MPa) and a hydrogen feed rate in the range of from 500 to 10,000 SCF/B (89.04 to 1780,9 liters H_2/liter feed)) in a hydroisomerization zone (R-2) in the presence of a fluorided Group VIII metal-on-alumina catalyst having (i) a bulk fluoride concentration ranging from 2 to 10 weight percent, wherein the fluoride concentration is less than about 3.0 weight percent at the outer surface layer to a depth less than one one-hundredth of an inch (0.254 mm), provided the surface fluoride concentration is less than the bulk fluoride concentration, (ii) an aluminum fluoride hydroxide hydrate level greater than 60 (e.g., at least about 100) where an aluminum fluoride hydrate level of 100 corresponds to the X-ray diffraction peak height of 5.66Å (0.566 nm) for a Reference Standard containing 0.6 wt.% Pt and 7.2 wt.% F on a support of gamma-alumina having a surface area of about 150 m^2/g and which Reference Standard is prepared by treating standard reforming grade gamma alumina having a surface area of about 150 m^2/g with platinum followed by single contact with an aqueous solution containing a high concentration of hydrogen fluoride followed by drying at about 300°F (148.9°C) and (iii) a N/Al ratio less than about 0.005;
(c) fractionating the effluent from step (b) in a fractionation zone (F-1) to produce a lubricating oil fraction boiling above 640°F (337.8°C) (e.g., above 700°F, 371.1°C) at atmospheric pressure; and
(d) dewaxing the lubricating oil fraction from step (c) in a dewaxing zone (D-1) and recovering a dewaxed lubricating oil having a viscosity index of at least 130 (e.g., at least 140) and a pour point less than about 0°F (-17.8°C), e.g., below -6°F (-21.1°C).

2. The process of claim 1 comprising contacting the isomerate from step (b) with hydrogen in the presence of a hydrofinishing catalyst comprising a Group VIII noble metal (e.g., platinum) on a refractory oxide base in a hydrofinishing zone (R-3) run at mild conditions comprising a temperature in the range of from 340 to 450°F (171.1 to 232.2°C) and a gauge pressure in the range of from 300 to 1500 psi (2.068 to 10.343 MPa) to reduce unsaturation of the isomerate and thereby improve its daylight stability and oxidation stability, and passing the hydrofinished material to step (c).

3. The process of claim 2 wherein the hydrofinishing catalyst comprises a fluorided Group VIII metal (e.g., platinum) on an alumina base.

4. The process of claim 2 or claim 3 wherein the hydrofinishing catalyst is a platinum-on-alumina catalyst of the type defined in step (b).

5. The process of any one of claims 1 to 4 wherein the Group VIII metal on the catalyst employed in step (b) is platinum.

6. The process of any one of claims 1 to 5 wherein said catalyst employed in step (b) contains from 0.3 to 0.6 weight percent platinum and from 5 to 8 weight percent fluoride.

7. The process of any one of claims 1 to 6 wherein the Fischer-Tropsch wax is subjected to severe hydrotreating conditions in step (a) including a temperature in the range of from 700°F to 750°F (371.1 to 398.9°C) and a hydrogen (gauge) pressure in the range of from 1000 - 1500 psig (6.895 to 10.343 MPa).

8. The process of any one of claims 1 to 7 wherein from about 10 - 35 wt% of the Fischer-Tropsch wax introduced into the hydroisomerization zone is converted to distillate and lighter products.

9. The process of any one of claims 1 to 8 comprising recovering a lubricating oil fraction in step (c) having a boiling point in the range of from 640 °F to 1000 °F (337.7 to 537.8 °C).

10. The process of any one of claims 1 to 9 comprising recovering a residual fraction from step (c) and recycling said residual fraction to the hydroisomerization zone.

Revendications

1. Procédé pour produire une huile lubrifiante ayant un indice de viscosité élevé et un point d'écoulement faible à partir d'une cire Fischer-Tropsch, procédé qui comprend:
(a) la mise en contact de la cire Fischer-Tropsch avec un catalyseur d'hydrotraitement (qui peut être non-sulfuré) et de l'hydrogène dans une zone d'hydrotraitement (R-1) dans des conditions d'hydro-traitement (comprenant une température dans la plage de 650 à 775 °F (343,3 à 412,8 °C), une pression d'hydrogène dans la plage de 500 à 2 500 psig (3,448 à 17,238 MPa), une vitesse de volume dans la plage de 0,1 à 2,0 V/V/H et un rapport hydrogène/alimentation dans la plage de 500 à 5 000 SCF/B (89,04 à 890,44 litres de H_2/litre d'alimentation)) pour réduire les teneurs en composés oxygénés et en traces de métaux de la cire et pour réaliser partiellement un hydrocraquage et une isomérisation de la cire;
(b) la mise en contact de la cire Fischer-Tropsch hydrotraitée de l'étape (a) avec l'hydrogène dans des conditions d'hydro-isomérisation (comprenant une température dans la plage de 500 à 750 °F (260 à 398,9 °C), une vitesse de volume d'alimentation dans la plage de 0,2 à 2,0 V/V/H, une pression manométrique dans la plage de 500 à 2 500 psig (3,448 à 17,238 MPa) et une teneur d'alimentation en hydrogène dans la plage de 500 à 10 000 SCF/B (89,04 à 1780,9 litres de H_2/litre d'alimentation)) dans une zone d'hydro-isomérisation (R-2) en présence d'un catalyseur de métal du groupe VIII fluoruré sur alumine ayant (i) une concentration en fluorure globale comprise entre 2 et 10% en poids, dans lequel la concentration en fluorure est inférieure à environ 3,0 pourcent en poids dans la couche superficielle externe à une profondeur inférieure à un centième de pouce (0,254 mm), pourvu que la concentration en fluorure superficiel soit inférieure à la concentration en fluorure globale, (ii) une teneur en hydrate d'hydroxyde de fluorure d'aluminium supérieure à 60 (par exemple, au moins environ 100) où une teneur en hydrate de fluorure d'aluminium de 100 correspond à la hauteur du pic à 5,66Å (0,566 nm) de diffraction aux rayons X pour un standard de référence contenant 0,6% en poids de Pt et 7,2% en poids de F sur un support d'alumine-gamma ayant une surface spécifique d'environ 150 m^2/g et dont le standard de référence est préparé par traitement d'alumine-gamma de qualité de reformage standard ayant une surface spécifique d'environ 150 m^2/g avec du platine suivi par un contact unique avec une solution aqueuse contenant une concentration élevée en fluorure d'hydrogène suivi par un séchage à environ 300 °F (148,9 °C) et (iii) un rapport N/Al inférieur à environ 0,005;
(c) le fractionnement de l'effluent de l'étape (b) dans une zone de fractionnement (F-1) pour produire une fraction d'huile lubrifiante bouillant au-dessus de 640 °F (337,8 °C) (par exemple, au-dessus de 700 °F, 371,1 °C) à la pression atmosphérique; et
(d) le décirage de la fraction d'huile lubrifiante de l'étape (c) dans une zone de décirage (D-1) et la récupération d'une huile lubrifiante décirée ayant un indice de viscosité d'au moins 130 (par exemple, au moins 140) et un point d'écoulement inférieur à environ 0 °F (-17,8 °C), par exemple en-dessous de -6 °F (-21,1 °C).

2. Procédé selon la revendication 1, comprenant la mise en contact de l'isomérat de l'étape (b) avec l'hydrogène en présence d'un catalyseur d'hydrofinition comprenant un métal noble du groupe VIII (par exemple, le platine) sur une base d'oxyde réfractaire dans une zone d'hydrofinition (R-3), effectuée dans des conditions douces comprenant une température dans la plage de 340 à 450 °F (171,1 à 232,2 °C) et une pression manométrique dans la plage de 300 à 1 500 psi (2,068 à 10,343 MPa) pour réduire l'insaturation de l'isomérat et en conséquence pour améliorer sa stabilité à la lumière du jour et à l'oxydation, et passage de la substance hydrofinie à l'étape (c).

3. Procédé selon la revendication 2, dans lequel le catalyseur d'hydrofinition comprend un métal fluoruré du groupe VIII (par exemple, le platine) sur une base d'alumine.

4. Procédé selon la revendication 2 ou la revendication 3, dans lequel le catalyseur d'hydrofinition est un catalyseur platine-sur-alumine du type défini à l'étape (b).

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le métal du groupe VIII sur le catalyseur employé dans l'étape (b) est le platine.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ledit catalyseur employé dans l'étape (b) contient de 0,3 à 0,6 pourcent en poids de platine et de 5 à 8 pourcent en poids de fluorure.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la cire Fischer-Tropsch est soumise aux conditions sévères d'hydrotraitement dans l'étape (a) comprenant une température dans la plage de 700°F à 750°F (371,1 à 398,9°C) et une pression manométrique d'hydrogène dans la plage de 1 000 à 1 500 psig (6,895 à 10,343 MPa).

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel d'environ 10 à 35% en poids de la cire Fischer-Tropsch introduite dans la zone d'hydro-isomérisation est convertie en distillat et produits plus légers.

9. Procédé selon l'une quelconque des revendications 1 à 8, comprenant la récupération d'une fraction d'huile lubrifiante dans l'étape (c) ayant un point d'ébullition dans la plage de 640°F à 1 000°F (337,7 à 537,8°C).

10. Procédé selon l'une quelconque des revendications 1 à 9, comprenant la récupération d'une fraction résiduelle de l'étape (c) et le recyclage de ladite fraction résiduelle à la zone d'hydro-isomérisation.

Patentansprüche

1. Verfahren zur Herstellung eines Schmieröls mit einem hohen Viskositätsindex und einem niedrigen Fließpunkt aus einem Fischer-Tropsch-Paraffin, bei dem:
(a) das Fischer-Tropsch-Paraffin mit einem Hydrobehandlungskatalysator (der unsulfidiert sein kann) und Wasserstoff in einer Hydrobehandlungszone (R-1) unter Hydrobehandlungsbedingungen (umfassend eine Temperatur im Bereich von 343,3 bis 412,8°C (650 bis 775°F), einen Wasserstoffüberdruck im Bereich von 3,448 bis 17,238 MPa (500 bis 2500 psig), einen Durchsatz im Bereich von 0,1 bis 2,0 V/V/Std. (Volumen Einsatzmaterial/Volumen Katalysator/Stunde) und eine Wasserstoffzuführungsgeschwindigkeit im Bereich von 89,04 bis 890,44 l H_2 pro Liter Einsatzmaterial (500 bis 5000 SCF/B)) kontaktiert wird, um die Mengen an Sauerstoff- und Spurenmetallmengen des Paraffins zu verringern und das Paraffin teilweise zu hydrocracken und zu isomerisieren,
(b) das hydrobehandelte Fischer-Tropsch-Paraffin aus Schritt (a) unter Hydroisomerisierungsbedingungen (umfassend eine Temperatur im Bereich von 260 bis 398,9°C (500 bis 750°F), einen Überdruck im Bereich von 3,448 bis 17,238 MPa (500 bis 2500 psig), einen Einsatzmaterialdurchsatz im Bereich von 0,2 bis 2,0 V/V/Std., eine Wasserstoffzuführungsgeschwindigkeit im Bereich von 89,04 bis 1780.9 l H_2 pro Liter Einsatzmaterial (500 bis 10 000 SCF/B)) in einer Hydroisomerisierungszone (R-2) in Gegenwart eines fluorierten, Metall der Gruppe VIII auf Aluminiumoxid enthaltenden Katalysators mit Wasserstoff kontaktiert wird, welcher (i) eine Fluoridgesamtkonzentration im Bereich von 2 bis 10 Gew.% aufweist, wobei die Fluoridkonzentration an der äußeren Oberflächenschicht bis zu einer Tiefe von weniger als 0,254 mm (100-stel eines Inch) geringer als etwa 3,0 Gew.% ist, vorausgesetzt, daß die Oberflächenfluoridkonzentration geringer als die Fluoridgesamtkonzentration ist, (ii) ein Aluminiumfluoridhydroxidhydratniveau größer als 60 (z.B. mindestens etwa 100) aufweist, wobei ein Aluminiumfluoridhydratniveau von 100 der Röntgenbeugungspeakhöhe von 0,566 nm (5,66 Å) für einen Referenzstandard entspricht, der 0,6 Gew.% Pt und 7,2 Gew.% F auf einem Träger aus Gamma-Aluminiumoxid mit einer Oberfläche von etwa 150 m²/g enthält und hergestellt worden ist, indem Standard Gamma-Aluminiumoxid mit Reformingqualität mit einer Oberfläche von etwa 150 m²/g mit Platin behandelt, anschließend einmalig mit einer eine hohe Konzentration Fluorwasserstoff enthaltenden, wäßrigen Lösung kontaktiert und dann bei etwa 148,9°C (300°F) getrocknet worden ist, und (iii) ein N/Al-Verhältnis von weniger als etwa 0,005 aufweist,
(c) das ausströmende Material aus Schritt (b) in einer Fraktionierungszone (F-1) fraktioniert wird, um eine Schmierölfraktion herzustellen, die oberhalb von 337,8°C (640°F) (z.B. oberhalb von 371,1°C, 700°F) bei Atmosphärendruck siedet, und
(d) die Schmierölfraktion aus Schritt (c) in einer Entparaffinierungszone (D-1) entparaffiniert und ein entparaffiniertes Schmieröl gewonnen wird, das einen Viskositätsindex von mindestens 130 (z.B.

mindestens 140) und einen Fließpunkt niedriger als etwa -17,8 °C (0 °F), z.B. unter -21,1 °C (-6 °F), aufweist.

2. Verfahren nach Anspruch 1, bei dem das Isomerat aus Schritt (b) in Gegenwart eines Hydroveredelungskatalysators, der ein Edelmetall der Gruppe VIII (z.B. Platin) auf einer feuerfesten Oxidbasis umfaßt, in einer Hydroveredelungszone (R-3), die unter milden Bedingungen betrieben wird, welche eine Temperatur im Bereich von 171,1 bis 232,2 °C (340 bis 450 °F) und einen Überdruck im Bereich von 2,068 bis 10,343 MPa (300 bis 1500 psi) umfassen, mit Wasserstoff kontaktiert wird, um den Gehalt des Isomerats an ungesättigte Stellen zu verringern und dadurch seine Tageslichtstabilität und Oxidationsstabilität zu verbessern, und das hydroveredelte Material zu Schritt (c) geleitet wird.

3. Verfahren nach Anspruch 2, bei dem der Hydroveredelungskatalysator ein fluoriertes Metall der Gruppe VIII (z.B. Platin) auf einer Aluminiumoxidbasis umfaßt.

4. Verfahren nach Anspruch 2 oder Anspruch 3, bei dem der Hydroveredelungskatalysator ein Platin-auf-Aluminiumoxid enthaltender Katalysator der in Schritt (b) definierten Art ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem das Metall der Gruppe VIII auf dem in Schritt (b) verwendeten Katalysator Platin ist.

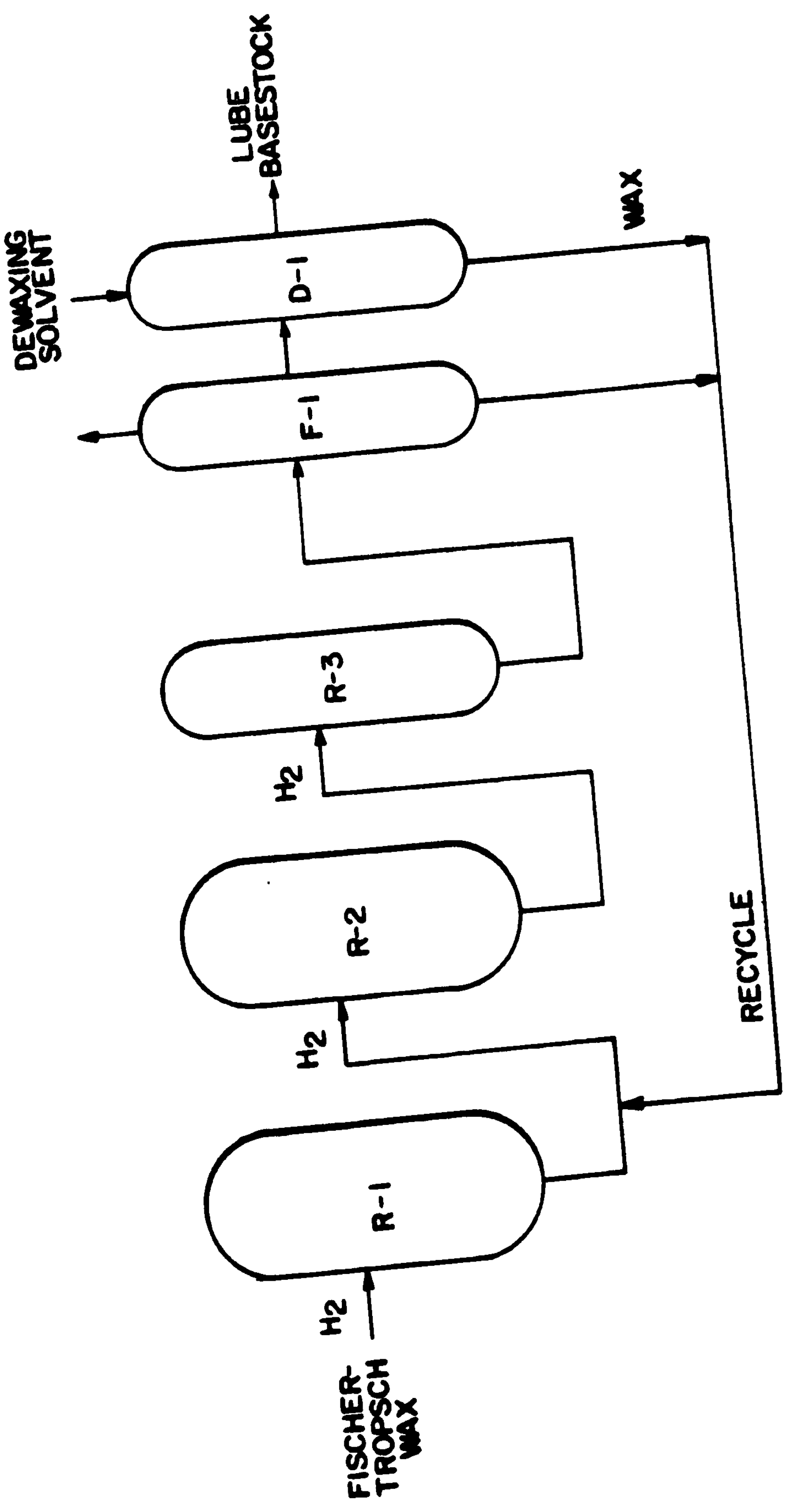
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem der in Schritt (b) verwendete Katalysator 0,3 bis 0,6 Gew.% Platin und 5 bis 8 Gew.% Fluorid enthält.

7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem das Fischer-Tropsch-Paraffin in Schritt (a) strengen Hydrobehandlungsbedingungen unterzogen wird, die eine Temperatur im Bereich von 371,1 bis 398,9 °C (700 °F bis 750 °F) und einem Wasserstoffüberdruck im Bereich von 6,895 bis 10,343 MPa (1000 bis 1500 psig) einschließen.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem etwa 10 bis 35 Gew.% des in die Hydroisomerisierungszone eingeführten Fischer-Tropsch-Paraffins in Destillat und leichtere Produkte umgewandelt wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, bei dem in Schritt (c) eine Schmierölfraktion gewonnen wird, die einen Siedepunkt im Bereich von 337,7 bis 537,8 °C (640 °F bis 1000 °F) aufweist.

10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem aus Schritt (c) eine Rückstandsfraktion gewonnen wird und die Rückstandsfraktion zur Hydroisomerisierungszone zurückgeführt wird.



LUBE BASESTOCK
DEWAXING SOLVENT
WAX
D-I
F-I
R-3
H2
R-2
H2
R-I
H2
FISCHER-TROPSCH WAX
RECYCLE